

New "turn-off" fluorescence sensors to detect vapors of nitro-explosives on the basis of 4,6-bis[5-(heteroaryl)thiophen-2-yl] substituted 5-(4-*tert*-butylphenyl)pyrimidines

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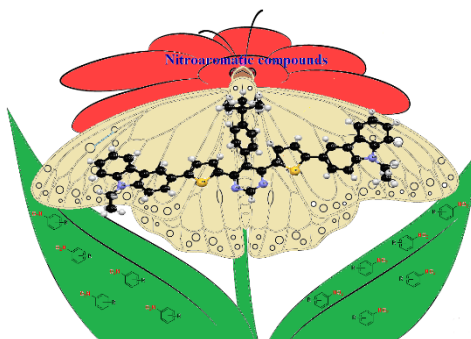
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Abstract

New D- π -A- π -D type dyes based on compounds of the pyrimidine family, bearing thiophene linkers, have been designed, synthesized and characterized. The fluorescence behavior of these fluorophores have been evaluated for fifteen nitro compounds. The detection limits for these fluorophores in relation to nitro explosives in acetonitrile solution proved to be in the range from 10^{-1} to 10^{-6} mol/L. The sensor prototypes for handheld sniffer «Nitroscan» (Plant «Promavtomatika», Ekaterinburg, Russia), based on these fluorophores, have been fabricated and used, as illustrated by reversible and sensitive fast detection of nitrobenzene in vapor phase concentrations up to 0.06 ppm.



Keywords: Pyrimidines, carbazoles, triphenylamines; pyrene, nitroaromatic explosives, fluorescence quenching

Introduction

Discovery of new materials and development of effective devices for detection of explosives has attracted world-wide attention, because it is critical for homeland security, civilian safety, and environmental protection.¹⁻⁵ Instrumental methods, which are generally used to detect nitro explosives, include gas chromatography coupled with mass spectrometry,⁶⁻⁸ nuclear quadrupole resonance,⁹ energy dispersive X-ray diffraction,¹⁰ and ion mobility spectrometry (IMS),^{11,12} but all these methods are rather expensive, and can hardly be made portable. In addition, many of these techniques require special equipment and/or need in pre-concentrating procedures.^{13,14}

On the other hand, there are a number of commercially available, portable (hand-held and stand-off) chemical detection sniffers (sensors working as an artificial dog's nose), exploiting advantage of materials, which are capable of detection of explosives through smell of these compounds.¹⁵ «Fido X2» (weighs 680 g), «Fido X3» (weighs 1.36 kg), and «Fido NXT» (weighs 1.36 kg) from FLIR Systems Inc. (Wilsonville, Oregon, USA)¹⁶ are the most famous lightweight, hand portable fluorescence polymer sensors for rapid detection of explosives, operating in many United States airports. «Nitroscan» (weighs 2.00 kg) is the Russian portable detector of nitro-explosives, produced by «Promavtomatika» Plant in collaboration with «UralProektAvtomatika» and «Security Intermolecular System» (Ekaterinburg, Russia).¹⁷ In this device, fluorescence-based sensors have been used, due to their high sensitivity, selectivity, simplicity, and a low cost in fabrication.

Organic materials, bearing electron-rich fragments, such as triphenylamine, carbazole or pyrene, conjugated with either monomeric or polymeric molecules, have received a considerable attention due to their promising properties as fluorescent chemosensors.¹⁸⁻²³ It is known, that π -deficient azaaromatic compounds, such as pyridines²⁴⁻²⁶ or pyrimidines,²⁷⁻³² can be used as electron-withdrawing units in the so-called "push-pull" luminophores. Such structures have been used as promising sensing materials for detection of a variety of nitroaromatics through fluorescence quenching.³³⁻⁴⁰

As a part of our research studies on pyrimidine-based π -conjugated systems, we envisaged that mixed π -conjugated 4,6-*bis*[5-(heteroaryl)-thiophen-2-yl]-5-(4-*tert*-butylphenyl) pyrimidines, consisting of the electron-donating part, presented by triphenylamine, carbazole or pyrene fragments, and the electron-withdrawing pyrimidine unit, would be a new class of push-pull fluorophores with improved sensitivity towards nitroaromatic compounds. Indeed, we have been motivated to synthesize D- π -A- π -D conjugates **7a-c**, in which electron-donating groups are attached to 4- and 6-positions of the pyrimidine ring via the thiophene spacer and 4-*tert*-butylphenyl substituent is incorporated at C-5 of pyrimidines. Although some 4,6-(hetero)aryl substituted pyrimidines have been synthesized,^{28,41} no reports on 4,6-*bis*(carbazol-3-yl) pyrimidines have so far been published.

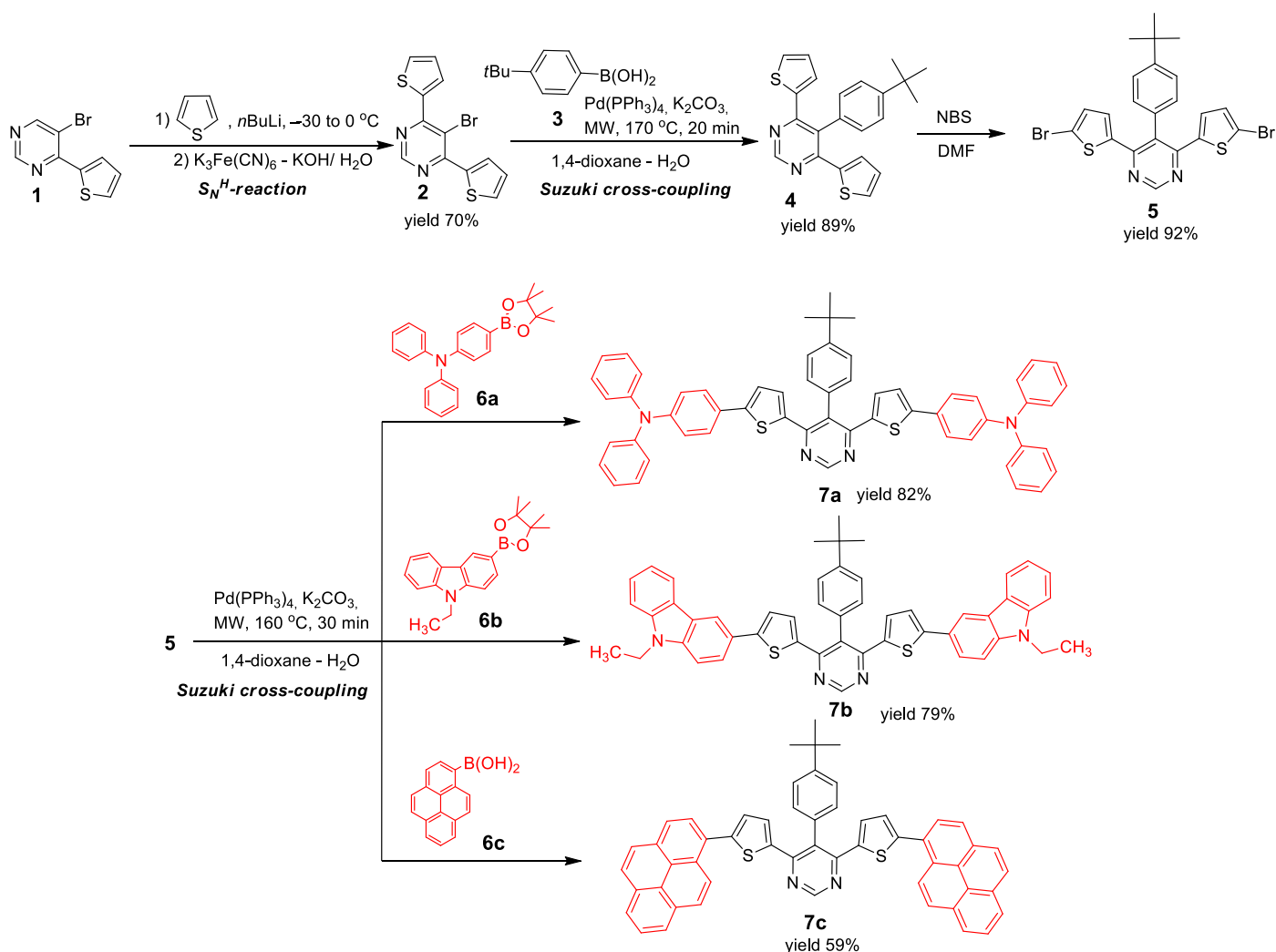
We describe herein the synthesis and the photophysical properties of **7a-c** on the basis of UV-vis and fluorescence spectral measurements. The sensitivity and selectivity to the presence of some nitroaromatic explosives in very small quantities, both in vapor and in solution phases, thus causing a significant quenching of the emission is also evaluated.

Results and Discussion

The starting material in the performed syntheses was 5-(4-*tert*-butylphenyl)-4,6-di(thiophen-2-yl)pyrimidine (**4**). To prepare compound **4** from readily available 5-bromo-4-(thiophen-2-yl)pyrimidine (**1**), a previously developed synthetic protocol involving nucleophilic aromatic substitution of hydrogen (for a better understanding of the

S_N^H -reactions, see the recently published review,⁴² and references, cited therein) and Suzuki cross-coupling has been used (Scheme 1).⁴³ Further bromination of pyrimidine **4** with 5 equiv. of *N*-bromosuccinimide (NBS) in DMF at room temperature gave 4,6-bis(5-bromothiophen-2-yl)-5-(4-*tert*-butylphenyl)pyrimidine (**5**) in 92% yield. Compound **5** can be coupled easily with the corresponding pinacol esters of 4-(diphenylamino)phenylboronic (**6a**), 9-ethyl-9*H*-carbazole-3-boronic (**6b**) acids or pyrene-1-boronic acid (**6c**) under microwave irradiation in 1,4-dioxane/H₂O in the presence of K₂CO₃ and Pd(PPh₃)₄, as catalyst. All reactions studied proved to afford the corresponding D- π -A- π -D dyes **7a-c** [where A – acceptor, the pyrimidine unit, D – a donating part, presented by triphenylamine, carbazole or pyrene fragments, and π -system is presented by a thienyl group] in 59-82% yields within the reaction time, not exceeding 30 min (Scheme 1).

The structural evidence for compounds **7a-c** has been provided by their spectral data, including ¹H and ¹³C NMR (see *Supporting Information*), and the data of high-resolution mass spectrometry. Furthermore, the structure of 3,3'-{5,5'-[5-(4-*tert*-butylphenyl)pyrimidine-4,6-diyl]bis(thiophene-5,2-diyl)}bis(9-ethyl-9*H*-carbazole) (**7b**) has been established unequivocally by X-ray crystallography analysis (Figure 1).



Scheme 1. Synthetic route to 4,6-bis[5-(heteroaryl)-thiophen-2-yl]-5-(4-*tert*-butylphenyl)pyrimidines (**7a-c**).

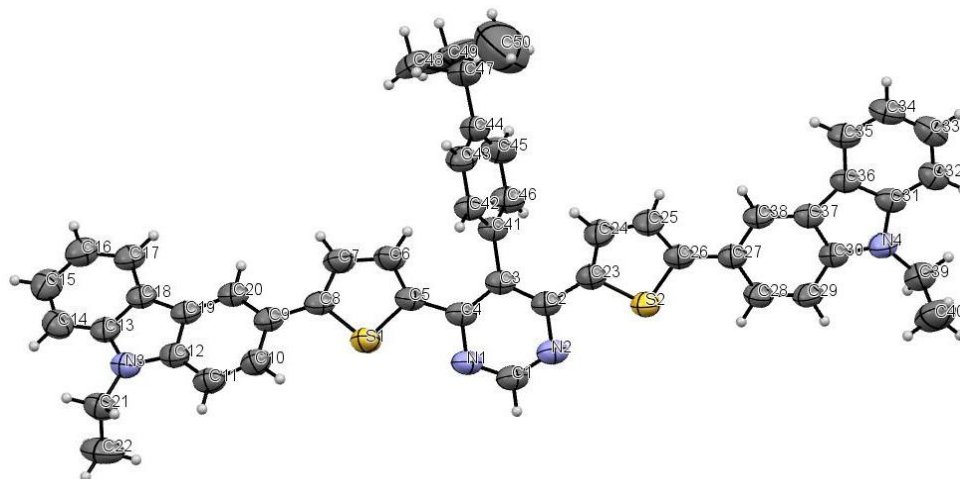


Figure 1. An ORTEP diagram of compound **7b**, showing 50% probability thermal ellipsoids.

Optical properties and fluorescence quenching studies in acetonitrile solution

A characteristic trait of this class of compounds is that their absorption and emission wavelengths can be adjusted by careful tuning of their molecular structures. To evaluate the effect of triphenylamine, carbazole and pyrene moieties on photophysical properties, the fluorescence excitation and emission spectra of **7a-c** have been recorded. The spectra are shown in Figure 2 and the main optical properties are given in Table 1.

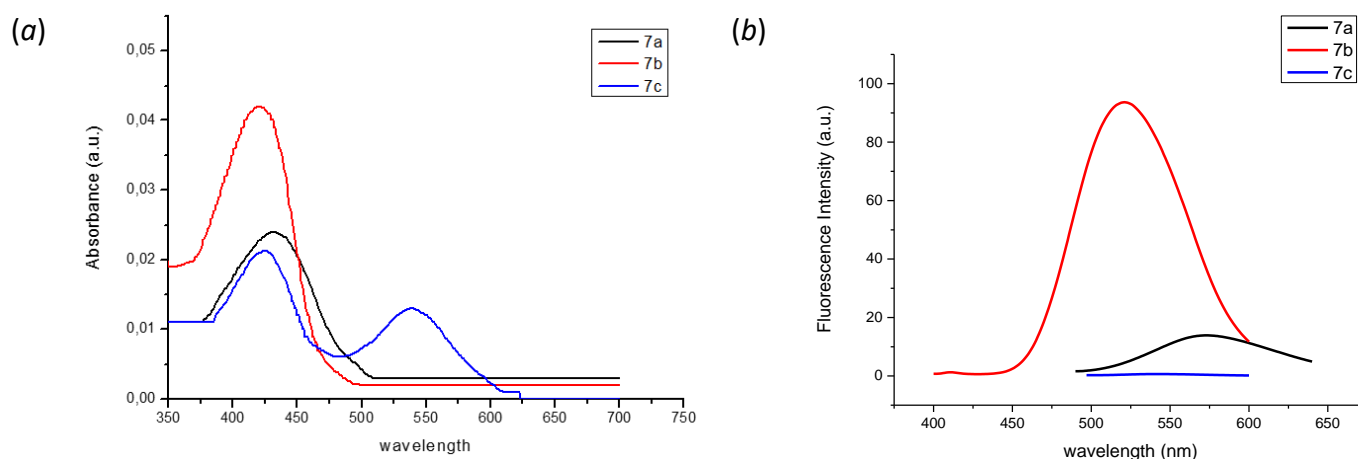


Figure 2. Absorption and emission spectra of fluorophores **7a-c**. (a) Absorption spectra of **7a-c** in CH_3CN . (b) Emission spectra of **7a-c** in CH_3CN .

Table 1. Photophysical data for fluorophores **7a-c** taken in acetonitrile

Fluorophores	Absorption $\lambda_{\text{max}}(\text{nm})/\epsilon$ ($10^3 / \text{M}^{-1} \text{cm}^{-1}$)	Fluorescence		Quantum yield (Φ)	Stokes shift $\Delta\nu_{\text{st}}/\text{cm}^{-1}$
		Excitation $\lambda_{\text{max}}(\text{nm})$	Emission $\lambda_{\text{max}}(\text{nm})$		
7a	433/23.00	433	572	0.04	5612
7b	412/43.00	412	519	0.07	5004
7c	430/18.00 528/12.00	528	541	0.003	455

Fluorophores **7a-c** have been established to show broad absorption maxima at the region of 412-528 nm ($\epsilon = 12000\text{--}43000\text{ M}^{-1}\cdot\text{cm}^{-1}$), which can be attributed to intramolecular charge-transfer excitation from the donating moiety to the pyrimidine ring (Table 1, Fig. 2a). The solutions of all compounds **7a-c** have moderate green-orange luminescence with emission maxima at 519–572 nm (Table 1, Fig. 2b); thus, relative quantum yields varies from 0.3% to 7.0%.

To evaluate an ability of the D- π -A- π -D type dyes **7a,b** on the basis of the pyrimidine scaffold to detect nitro-explosives, the fluorescence measurements of **7a,b** have been carried out in acetonitrile solutions, containing measured quantities of nitroaromatic compounds, as quenchers of the fluorescence (Figure 3). It should be noted that the fluorescence measurements of compound **7c** in acetonitrile solutions at the presence of nitro-explosives was not carried out by reason of poor relative quantum yield <1%. However, compound **7c** was possessed of the satisfactory fluorescence in solid state (see Figure S1 in *Supplementary Material*) and it was also used for detection of nitroaromatic vapors.

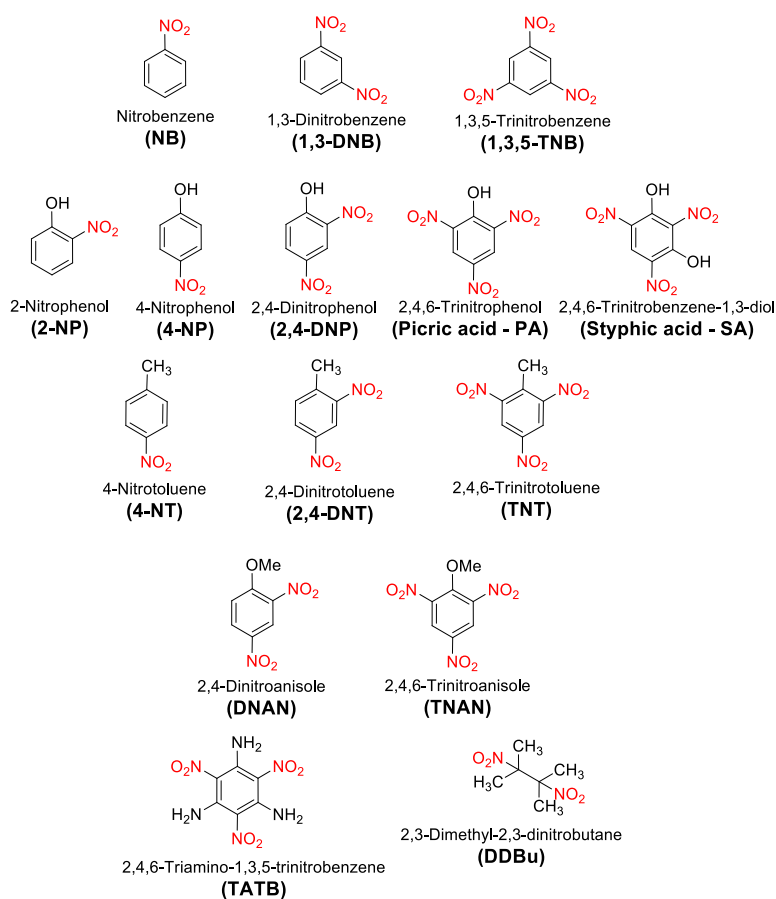


Figure 3. Structures of used quenchers.

Figures S2 and S3 (see *Supplementary Material*) show the fluorescence emission spectra of **7a,b** in the presence of various concentrations of the analytes with 412 or 433 nm, as the excitation wavelength. All nitroaromatics appear to act as fluorescence quenchers for compounds **7a-c** (Table 2). Visual changes of color for solutions of fluorophores **7a,b** with additives of different quenchers are shown in Figures S4 and S5 (see *Supporting Information*). Fluorophore **7b** have higher values of the quenching constants K_{SV} and detection limits (DL) (see Table 2) than fluorophore **7a**, which are in a good agreement with values of quantum yields (see Table 1).

Quenching efficiency was calculated by using the formula $(I_0 - I) / I_0 \times 100\%$, where I_0 and I are the fluorescence intensities of fluorophores **7a** and **7b** before and after exposure to a particular analyte, respectively. Figure 4 shows quenching efficiency of various nitroaromatics and DDBu towards fluorophores **7a,b**.

It can be seen that this fluorophores **7a,b** exhibit fast and sensitive response to nitrobenzene, and nearly 64-85% of the original emission values are quenched by these fluorophores, when their concentrations reach 5×10^{-7} mol/L. In other words, the most effective quencher proved to be nitrobenzene, while other NACs are less effective ones (Figs. 4, S4 and S5, entry 4). In our opinion, the most reasonable explanation of this fact is a steric hindrances increase with an addition of substituents in benzene ring.

Table 2. Quenching constants (K_{SV}) and detection limits (DL) of NB, 1,3-DNB, 1,3,5-TNB, 2-NP, 4-NP, 2,4-DNP, PA, SA, 4-NT, 2,4-DNT, TNT, DNAN, TNAN, TATB and DDBu towards fluorophores **7a,b** in CH_3CN .

Nitro-compound	$K_{SV}, \text{M}^{-1} / \text{DL}, \text{mol} \times \text{L}^{-1}$	
	Fluorophore 7a	Fluorophore 7b
NB	1443 / 7.98×10^{-3}	3509 / 6.64×10^{-6}
1,3-DNB	293 / 2.92×10^{-2}	1138 / 9.53×10^{-6}
1,3,5-TNB	274 / 4.20×10^{-2}	520 / 2.32×10^{-5}
2-NP	75 / 1.54×10^{-1}	428 / 2.39×10^{-5}
4-NP	205 / 5.62×10^{-2}	363 / 3.16×10^{-5}
2,4-DNP	159 / 7.22×10^{-2}	156 / 5.30×10^{-5}
PA	160 / 7.30×10^{-2}	195 / 8.68×10^{-5}
SA	268 / 4.29×10^{-2}	802 / 1.63×10^{-5}
4-NT	350 / 3.29×10^{-2}	124 / 6.20×10^{-5}
2,4-DNT	314 / 3.67×10^{-2}	83 / 8.99×10^{-5}
TNT	67 / 1.71×10^{-1}	245 / 2.68×10^{-5}
DNAN	114 / 1.01×10^{-1}	224 / 4.51×10^{-5}
TNAN	113 / 1.00×10^{-1}	111 / 7.35×10^{-5}
TATB	605 / 1.90×10^{-2}	135 / 4.08×10^{-5}
DDBu	466 / 2.47×10^{-2}	92 / 8.46×10^{-5}

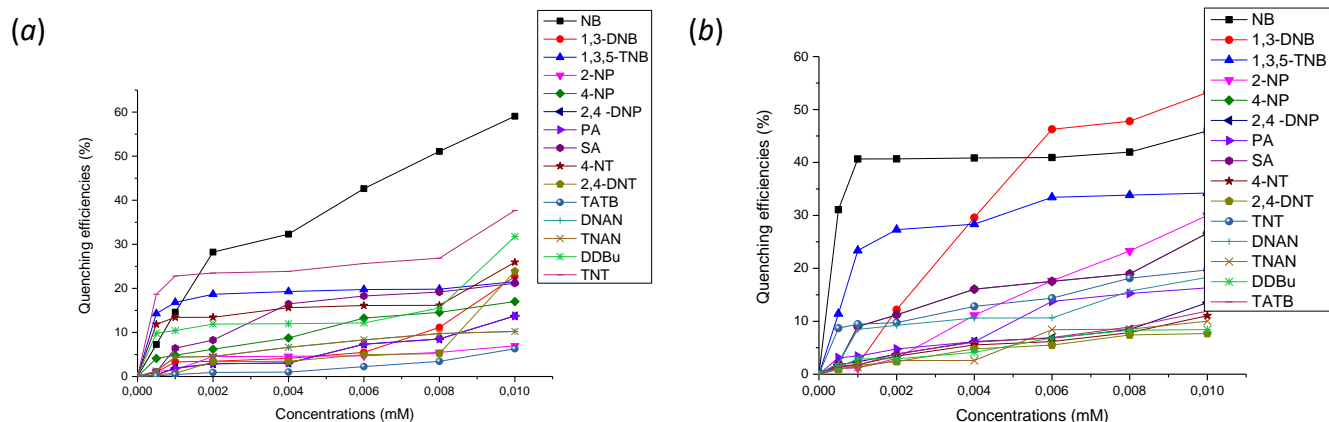


Figure 4. The plot of quenching efficiencies of NB, 1,3-DNB, 1,3,5-TNB, 2-NP, 4-NP, 2,4-DNP, PA, SA, 4-NT, 2,4-DNT, TNT, DNAN, TNAN, TATB relative to fluorophores **7a** (a) and **7b** (b) at mM level.

The linear relationship for the Stern-Volmer plot (in the range of concentrations from 0 to 2×10^{-6} M) (Figures S6 and S7 in *Supporting Information*) and similarity of structures with linear and V-shaped push-pull pyrimidines,^{35,40} bearing triphenylamine and carbazole as electron-donating fragment, suggests a high role of static type interactions for the quenching process.

Application of sensors in detecting of the nitroaromatic vapors

Nitrobenzene (NB) is mainly consumed in production of aniline, which is a precursor to rubber chemicals, pesticides, dyes (azo dyes), explosives, and pharmaceuticals. As a chemical material, it is also used in shoes and floor polishes, leather dressings, paints, organic solvents, etc. Also it is known, that NB is a highly toxic and carcinogenic agent (value of maximal allowable concentration $3 \mu\text{g}/\text{m}^3$), which is readily absorbed through the skin. Therefore, both environment and human health issues, caused by application of NB, have attracted a great attention of scientific community.⁴⁴ As mentioned, 2,4,6-trinitrotoluene (TNT) plays an important role not only in the military field, as a highly explosive material, but it is a highly toxic environment pollutant.⁴⁵ Many improvised explosive devices are fabricated by using impure TNT, in which the major impurity is 2,4-DNT used as the starting material for TNT synthesis. Notably, that sensing of nitroaromatic explosives is rarely applied to solutions or extracts.

We have decided to use NB, 2,4-DNT and TNT as model substances to evaluate their detection in vapor phase. To realize this, we have implemented the real-time solid-gas monitoring of nitrobenzene vapor by using a sensor with each of fluorophores **7a-c** on the basis of non-woven spunlace fabric placed in the portable sniffer «Nitroscan» (all details of sensor fabrication are reported in the Experimental Part).

At the first step, nitrobenzene $2.5 \mu\text{L}$ (3 mg) in CH_3CN $100 \mu\text{L}$ has been sprayed by a syringe in a hermetic glove-box ($0.8 \text{ m} \times 0.6 \text{ m} \times 0.4 \text{ m}$) and kept in this box during 12 h at room temperature to achieve a maximal allowable concentration (0.6 ppm) of nitrobenzene. It has been shown that all sensors **7a-c** are capable of a fast reversible self-recovery after interruption of exposure to nitroaromatic explosive. Reversibility of the sensing process for sensors on the basis of fluorophores **7a-c** 0.6 ppm NB vapor was examined by using the following procedure: The device «Nitroscan», bearing a sensor, was inserted into a glove box with saturated NB vapor for 50 s, and then the fluorescence intensity was recorded. After that, the device was removed from the box for 50 s, and the ambient room air was pumped automatically through the sensor in device. The recovered fluorescence efficiency of the sensor was measured. The sensing and pumped process was repeated 5 times, and the results obtained are shown in Figure 5.

Evaluation of the process at various lower concentrations of NB shows that all sensors **7a-c** have a high sensitivity up to 0.6 NB (Figure 5). Furthermore, fluorophore **7b** can detect nitrobenzene at 6 ppb concentration on air that is in a good agreement with a quenching evaluation in solution.

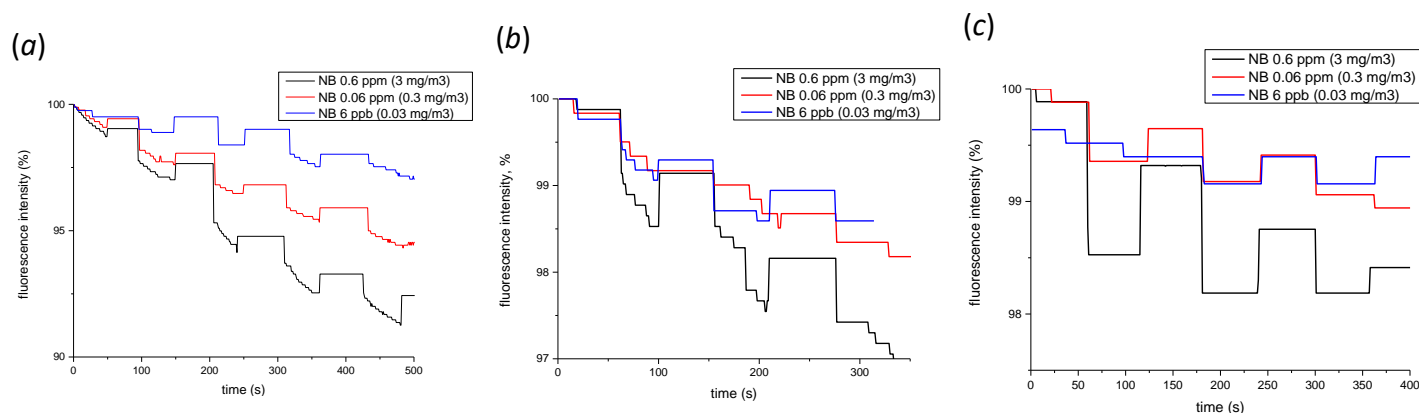


Figure 5. Fluorescent recovery cycles for the sensors on the basis of compounds **7a** (a), **7b** (b) and **7c** (c) in device «Nitroscan» with exposure to NB vapor in a range of concentration from 0.6 ppm to 6 ppb.

Similar protocol was used for detection of 2,4-DNT and TNT vapors at low concentrations by sensors **7a-c**. The results are summarized in Figures 6 and 7. It was found, that fluorophores can satisfactory detect 2,4-DNT and TNT vapors at concentrations higher than 0.13 ppm and 0.05 ppm, respectively. As shown in Figures 5-7, the quenching efficiency reaches remarkable values after exposing the device with any type of sensor in the box for 100 s but the recovered fluorescence intensity is decreasing with each next cycle.

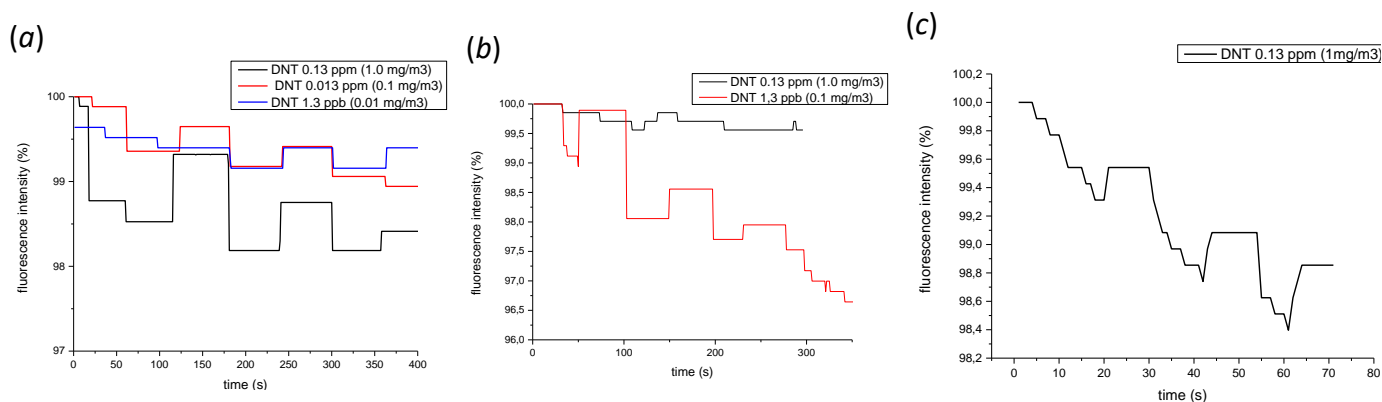


Figure 6. Fluorescent recovery cycles for the sensors on the basis of compounds **7a** (a), **7b** (b) and **7c** (c) in device «Nitroscan» with exposure to 2,4-DNT vapor in a range of concentration from 0.13 ppm to 1.3 ppb.

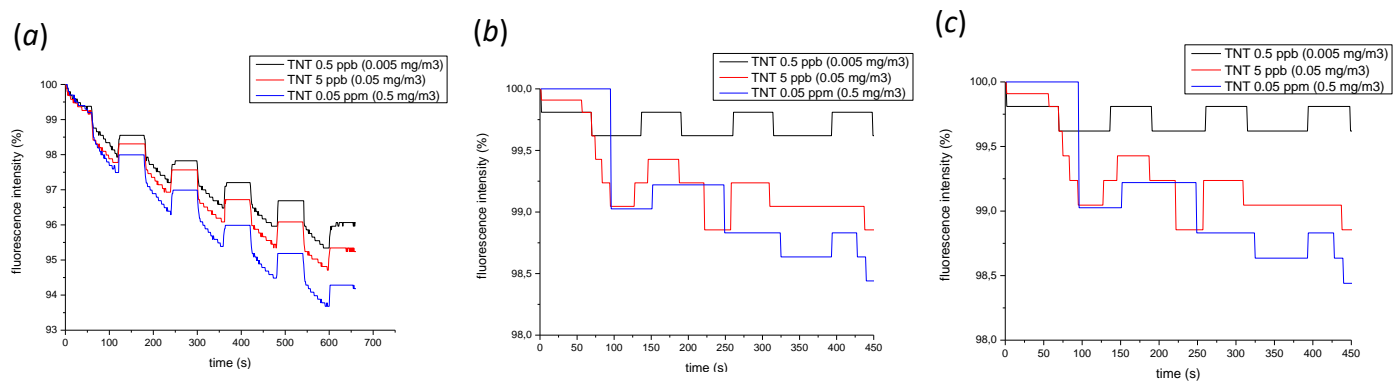


Figure 7. Fluorescent recovery cycles for the sensors on the basis of compounds **7a** (a), **7b** (b) and **7c** (c) in device «Nitroscan» with exposure to TNT vapor in a range of concentration from 0.05 ppm to 0.5 ppb.

To investigation the selectivity and sensitivity for the sensors **7a-c** we compared the quenching efficiencies at the presence of maximum allowable concentrations of NB, 2,4-DNT and TNT (0.6, 0.13 and 0.05 ppm, respectively)⁴⁶ and saturated vapors of some interferents, such as ethanol, ethylene glycol, acetone, acetic acid, toluene, phenol, and 1,2-dichlorobenzene (see Figure 8). As expected, sensors **7a** and **7b** show a good selectivity to NB in comparison with other explosives and interferents, since their quenching sensitivities are weaker in these vapors that in NB.

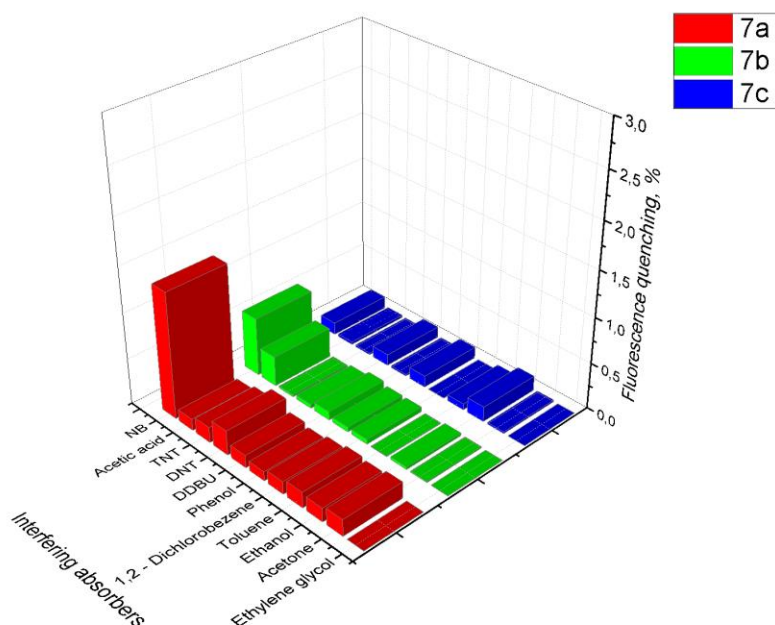


Figure 8. Sensor's **7a-c** fluorescence quenching (%) in first cycle towards various nitro-explosives and volatile interferents at room temperature.

Conclusions

Three dyes of the D- π -A- π -D type on the basis of pyrimidines, bearing thiophene π -linkers and various electron-donative fragments, have been studied, as sensing fluorophores. All dyes demonstrate a high sensitivity towards nitroaromatic explosives.

Selective fluorescence quenching response, including a sharp color change under UV lamp (especially for NB), makes these fluorophores into solution to be promising fluorescence sensor materials for nitroaromatic explosives with the detecting limit up to 10^{-6} mol/L, as estimated in experiments with NB.

Furthermore, the compounds obtained can be regarded as good sensing materials for the handheld sniffer «Nitroscan» (Plant «Promavtomatika», Ekaterinburg, Russia), since they exhibit a good potential, and pretend to be fast-response and highly sensitive sensors for detection of NB in vapors.

The present study can be regarded as a significant step to develop a new series of push-pull type sensing fluorophores with the pyrimidine core.

Experimental Section

General. All reagents and solvents were obtained from commercial sources and dried by using standard procedures before use. Nitroaromatic explosives, including 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (1,3,5-TNB), 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), picric acid (PA), styphnic acid (SA), 4-nitrotoluene (4-NT), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), 2,4-dinitroanisole (DNAN), 2,4,6-trinitroanisole (TNAN) and 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) were of analytical grade and used directly without further purification. (*Caution:* All nitro-containing compounds used in the present study are high explosives and should be handled only in small analytical quantities.)

The solvents (1,4-dioxane and H₂O) for the Suzuki cross-coupling reaction were deoxygenated by bubbling argon for 1h.

¹H and ¹³C NMR spectra were recorded on an AVANCE-500 instruments using Me₄Si as an internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. High-resolution mass spectrometry was performed using a Bruker maXis Impact HD spectrometer. Melting points were determined on Boetius combined heating stages and were not corrected.

Flash-column chromatography was carried out using Alfa Aesar silica gel 0.040-0.063 mm (230–400 mesh), eluting with ethyl acetate-hexane. The progress of reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia), in which the spots were visualized with UV light (λ 254 or 365 nm).

UV–vis spectra were recorded for a 1×10^{-5} M acetonitrile solution with Shimadzu UV-2401PC spectrophotometer. Fluorescence spectra measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. Quantum yields (Φ) were estimated with 1N H₂SO₄ solution of quinine bisulfate ($\Phi = 0.55$) as a reference.⁴⁷

The fluorescence quenching studies were carried out in acetonitrile. For each analyte, the typical test procedure was as follows: 2.5 mL of acetonitrile solution of one of the fluorophores (1.0×10^{-5} mol/L) was drawn and placed in a quartz cell of the standard size. Without analyte the fluorescence spectrum of pure fluorophore was first recorded. Subsequently, different amounts of analyte were added respectively in the cell. Each time after full mixing the analyte with fluorophore, the fluorescence spectrum was registered. The plots of I_0/I values of the quenching systems as functions of quencher concentrations ($[Q]$) were well described by the Stern–Volmer equation, $I_0/I = 1 + K_{sv}[Q]$, where I_0 and I are fluorescence intensities without and in the presence of analyte. The detection limits were calculated by use literature procedure (see details in *Supporting Information*).³⁵

To investigate detection of nitroaromatic explosives in vapor phase the original device «Nitroscan» (see Fig. S8) has been used. «Nitroscan» was produced by «Promautomatika» Plant in collaboration with «UralProektAvtomatika» (Ekaterinburg, Russia) and «Security Intermolecular System» (Ekaterinburg, Russia). The instrument is based on registration of excited steady-state luminescence quenching. Sensors for this device were obtained by application of a dye solution on the cellulose matrix. Reduction of sensor's luminescence intensity takes place due to an interaction of explosive vapors containing in the air. The decrease rate of the luminescence intensity indicates at the concentration of vapors. To study luminescent properties of the sensor element, its luminescence spectra excited by photons with energies in the range 280–425 nm were measured. The excitation photoluminescence spectra for luminescence bands of the sensor element were also measured. Excitation source was light emitting diode (375 nm) and luminescent signal receiver was a photodiode (430 - 650 nm) in the device designed. The device was operating under control of the program algorithm, which provides multiple operating modes (configuration, calibration, measurement etc.). The advantages of this device are autonomic power, a low weight and small sizes, as well as simplicity of operations for measurements. The calibration of the device «Nitroscan» was carried out with using of internal software. The fluorescence

measurements (excited at 375 nm) in solid phase were performed in device «Nitroscan» connected with a computer. More details about operation of the device «Nitroscan» are in reference.⁴⁸

The sensor for detection of NACs in vapor phase has been designed as cartridge. The cartridge has two parts which are connected at the contour of the framework. The non-woven spunlace fabric has been used as a porous substrate (70% viscose, 30% polyester, Industrial Spunlace purchased from Afalina Co., Ltd., Russia) for the fabrication of sensor. A piece of non-woven spunlace (50 mm in diameter) was immersed in the fluorophore solution with a concentration 1.0×10^{-3} M for 5 min. Then non-woven dry wipe or spunlace with immobilized fluorophore **7a** (**7b** or **7c**) was removed from the solution and dried at 70–80 °C for 30 min. To demonstrate its application as a fluorescence sensor for NACs detection, the obtained non-woven spunlace was placed in cartridge.

According to the general sanitary requirements for the working zone air of the Russian code for occupational safety, nitrobenzene (NB), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) were found to have had a maximal allowable concentrations (MAC) of 3 mg/m³ [0.60 ppm], of 1 mg/m³ [0.13 ppm], and 0.5 mg/m³ [0.05 ppm], respectively.⁴⁶

Nitrobenzene 5.8×10^{-4} g was dissolved in CH₃CN 10 mL. To detect of vapor of the nitroaromatic explosive, the aliquots 100 µL and 10 µL of the obtained nitrobenzene solution were sprayed by a syringe in a hermetic glove-box (0.8 m × 0.6 m × 0.4 m) and kept in this box during 12 h at room temperature to achieve respectively a 0.01 (0.03 mg/m³ or 6 ppb) and 0.001 (0.003 mg/m³ or 0.6 ppb) of maximal allowable concentrations of nitrobenzene. DNT 1.9×10^{-4} g was dissolved in CH₃CN 10 mL. To detect of vapor of the nitroaromatic explosive, the aliquot 100 µL of the obtained DNT solution was sprayed by a syringe in a hermetic glove-box (0.8 m × 0.6 m × 0.4 m) and kept in this box during 12 h at room temperature to achieve a 0.1 (0.1 mg/m³ or 1.3 ppb) of maximal allowable concentrations of TNT.

Similarly, TNT 1.0×10^{-4} g was dissolved in CH₃CN 10 mL. To detect of vapor of the nitroaromatic explosive, the aliquots 100 µL and 10 µL of the obtained TNT solution were sprayed by a syringe in a hermetic glove-box (0.8 m × 0.6 m × 0.4 m) and kept in this box during 12 h at room temperature to achieve respectively a 0.1 (0.05 mg/m³ or 5 ppb) and 0.01 (0.005 mg/m³ or 0.5 ppb) of maximal allowable concentrations of TNT.

To detect the vapor of interferents (15 ml), such as ethanol, ethylene glycol, acetone, acetic acid, toluene, phenol, and 1,2-dichlorobenzene, their placed in a hermetic glove-box (0.8 m×0.6 m×0.4 m). Interferent was kept in this box during 12 hours at room temperature until saturated vapor was reached.

A suitable crystal of **7b** was selected and XRD analysis was performed on a Xcalibur diffractometer on standard procedure (MoK_α graphite-monochromated irradiation, ω -scanning with 1° steps). The empirical absorption correction was applied. Using Olex2⁴⁹, the structure was solved with the SHELXS⁵⁰ structure solution program and refined with the SHELXL⁵⁰ refinement program using full-matrix least-squares on F² method in anisotropic approximation for non-hydrogen atoms. Deposition number CCDC 1570333 for **7b** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4,6-bis(5-Bromothiophen-2-yl)-5-(4-tert-butylphenyl)pyrimidine (5). NBS (890 mg, 5.0 mmol) was added to a solution of 5-(4-tert-butylphenyl)-4,6-di(thiophen-2-yl)pyrimidine (**4**) (377 mg, 1.0 mmol) in DMF (10 mL) at room temperature. Then the mixture was stirred for 24 h at room temperature. The reaction mixture was diluted with H₂O and the precipitate formed was filtered, washed with H₂O, and air-dried. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:1). The product **5** was isolated as a yellow powder (492 mg, 92%), mp 172–174 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.97 (s, 1H), 7.65–7.54 (m, 2H), 7.24–7.20 (m, 2H), 6.77 (d, *J* 4.2 Hz, 2H), 6.23 (d, *J* 4.2 Hz, 2H), 1.44 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 157.0, 156.6, 153.6,

144.1, 132.3, 131.4, 131.0, 129.1, 127.4, 125.1, 119.0, 35.0, 31.4. Calcd. for $C_{22}H_{18}Br_2N_2S_2$ (534.34): C 49.45, H 3.40, N 5.24. Found C 49.55, H 3.24, N 5.37. HRMS (ESI): m/z calcd for $C_{22}H_{19}Br_2N_2S_2$: 534.9336 $[M+H]^+$; found: 534.9333.

General procedure for the synthesis of 4,6-bis[5-(heteroaryl)-thiophen-2-yl]-5-(4-*tert*-butylphenyl)pyrimidines (7a-c). A solution of K_2CO_3 (138 mg, 1.0 mmol) in H_2O (2 mL) was added to a mixture of 4,6-bis(5-bromothiophen-2-yl)-5-(4-*tert*-butylphenyl)pyrimidine (**5**) (107 mg, 0.2 mmol) and pinacol ester 4-(diphenylamino)phenylboronic (**6a**) acid [pinacol ester 9-ethyl-9*H*-carbazole-3-boronic (**6b**) acid or pyrene-1-boronic acid (**6c**)] (0.44 mmol) and $Pd(PPh_3)_4$ (23 mg, 10 mol %) in 1,4-dioxane (4 mL). The resulting mixture was irradiated in a microwave apparatus at 160 °C (250 W) for 30 min. After that solvent was distilled off *in vacuo*, and the residue was purified by flash column chromatography (hexane/ethyl acetate, 1:2) to afford the desired cross-coupling products (**7a**, **7b** or **7c**).

4,4'-[5,5'-[5-(4-*Tert*-butylphenyl)pyrimidine-4,6-diyl]bis(thiophene-5,2-diyl)]bis(*N,N*-diphenylaniline) (7a). Yield 142 mg (82%), yellow powder, mp 242–244 °C. 1H NMR (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.69–7.65 (m, 2H), 7.63 (d, J 8.1 Hz, 2H), 7.55 (m, 1H), 7.47 (dd, J 7.5, 2.5 Hz, 2H), 7.43 (d, J 8.6 Hz, 4H), 7.32–7.24 (m, 5H), 7.11 (d, J 7.8 Hz, 8H), 7.07–6.99 (m, 8H), 6.93 (d, J 4.1 Hz, 2H), 6.35 (d, J 4.1 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 156.6, 148.6, 149.0, 147.3, 140.9, 133.5, 132.3, 132.1, 132.1, 131.93, 131.90, 129.4, 128.5, 128.4, 127.4, 127.2, 126.6, 124.8, 123.4, 123.1, 123.0, 35.0, 31.5. Calcd. for $C_{58}H_{46}N_4S_2$ (863.17): C 80.71, H 5.37, N 6.49. Found C 80.94, H 5.24, N 6.57. HRMS (ESI): m/z calcd for $C_{58}H_{47}N_4S_2$: 863.3237 $[M+H]^+$; found: 863.3236.

3,3'-[5,5'-[5-(4-*Tert*-butylphenyl)pyrimidine-4,6-diyl]bis(thiophene-5,2-diyl)]bis(9-ethyl-9*H*-carbazole) (7b). Yield 121 mg (79%), dark yellow powder, mp 259–261 °C. 1H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.32 (d, J 1.6 Hz, 2H), 8.07 (d, J 7.7 Hz, 2H), 7.72 (d, J 1.7 Hz, 1H), 7.71–7.66 (m, 3H), 7.52–7.45 (m, 2H), 7.40 (d, J 8.1 Hz, 2H), 7.37 (d, J 8.3 Hz, 4H), 7.25 (m, 2H), 7.09 (d, J 4.1 Hz, 2H), 6.45 (d, J 4.1 Hz, 2H), 4.36 (q, J 7.2 Hz, 4H), 1.52 (s, 9H), 1.44 (t, J 7.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6, 156.7, 153.0, 150.4, 140.6, 140.5, 139.9, 133.7, 132.4, 129.6, 127.3, 126.1, 125.2, 125.0, 124.0, 123.4, 122.89, 122.88, 120.5, 119.3, 118.0, 108.8, 108.7, 37.7, 35.0, 31.6, 13.8. Calcd. for $C_{50}H_{42}N_4S_2$ (763.05): C 78.71, H 5.55, N 7.43. Found C 78.84, H 5.44, N 7.57. HRMS (ESI): m/z calcd for $C_{50}H_{43}N_4S_2$: 763.2924 $[M+H]^+$; found: 763.2910.

5-(4-*Tert*-butylphenyl)-4,6-bis[5-(pyren-1-yl)thiophen-2-yl]pyrimidine (7c). Yield 92 mg (59%), yellow powder, mp 304–306 °C. 1H NMR (500 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.51 (d, J 9.3 Hz, 2H), 8.24–8.16 (m, 6H), 8.13–8.06 (m, 8H), 8.06–8.00 (m, 2H), 7.74 (d, J 8.2 Hz, 2H), 7.48 (d, J 8.2 Hz, 2H), 7.15 (d, J 3.9 Hz, 2H), 6.66 (d, J 3.9 Hz, 2H), 1.47 (s, 9H). The ^{13}C NMR spectra of compound **7c** could not be obtained due to the poor solubility of this compound in deuteriated solvents. Calcd. for $C_{54}H_{36}N_4S_2$ (777.03): C 83.47, H 4.67, N 3.61. Found C 83.28, H 4.84, N 3.49. HRMS (ESI): m/z calcd for $C_{54}H_{37}N_4S_2$: 777.2391 $[M+H]^+$; found: 777.2393.

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Supplementary Material

Additional supporting information can be found in the online version of this article at the publisher's website.

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